

Andrew Liehr and the structure of Jahn-Teller surfaces

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Andrew Liehr and the structure of Jahn-Teller surfaces

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Abstract. The present article is an attempt to draw attention to a seminal work by Andrew Liehr “Topological aspects of conformational stability problem” [1, 2] issued more than half century ago. The importance of this work stems from two aspects of static Jahn-Teller and pseudo-Jahn-Teller problems fully developed by the author. First, the work of Liehr offers an almost complete overview of adiabatic potential energy surfaces for most known Jahn-Teller problems including linear, quadratic and higher-order vibronic couplings. Second, and most importantly, it identifies the factors defining the structure of Jahn-Teller surfaces. Among them, one should specially mention the minimax principle stating that the distorted Jahn-Teller systems tend to preserve the highest symmetry consistent with the loss of their orbital degeneracy. We believe that the present short reminiscence not only will introduce a key Jahn-Teller scientist to the young members of the community but also will serve as a vivid example of how a complete understanding of a complex problem, which the Jahn-Teller effect certainly was in the beginning of 1960s, can be achieved.

1. Introduction

After the publication of the Jahn-Teller theorem in 1937 [3, 4], there was a period of almost two decades during which the Jahn-Teller effect practically did not attract attention except via a few albeit very important publications [5, 6, 7, 8]. The burst of interest for Jahn-Teller effect begins with the works of Moffitt and Liehr [9, 10], Moffitt and Thorson [11], Öpik and Pryce [12], Liehr and Ballhausen [13, 14] and Longuet-Higgins et al. [15] in the second half of 1950s. In this “golden” period, Andrew Liehr made seminal contributions which initiated several directions in Jahn-Teller research. He was one of the authors who first described theoretically the nuclear dynamics (dynamical Jahn-Teller effect) and the effect of quadratic vibronic coupling in Jahn-Teller systems [10]. He also was one of the first who identified the Jahn-Teller splitting of the spectroscopic bands [9]. However his most important contribution is related to the investigation of static Jahn-Teller problems and the identification of the main factors defining the structure of Jahn-Teller surfaces. His research in this domain, as well as of other authors at that time, was reviewed in a more than a hundred pages paper comprising the treatment of static Jahn-Teller (Part I) [1] and pseudo-Jahn-Teller (Part II) [2] problems. This work represents the first comprehensive review on Jahn-Teller effect and still remains the most complete overview of static Jahn-Teller effect. In this work, Andrew Liehr gives adiabatic potential energy surfaces (APES) for almost all known Jahn-Teller problems including linear, quadratic and higher-order vibronic couplings. He also identifies the factors influencing the structure of Jahn-Teller surfaces, among which the minimax principle is of paramount importance. In the present article we overview



and discuss these two basic aspects of the Liehr's work.

2. Adiabatic potential energy surfaces of Jahn-Teller problems

In the Part I [1], Liehr derived the analytical expressions for APES of almost all Jahn-Teller systems. His approach was to show specific systems and to visualize the APES and the pseudorotation of the Jahn-Teller distortions corresponding to nuclear motion at the bottom of the APES.

Liehr starts by considering the Renner-Teller effect in linear systems (C_2H_2 and triatomic molecule), and then investigates the vibronic problems of two-dimensional hydrocarbon molecules with axial symmetry (C_nH_n , $n = 3, 4, \dots, 8$). Since the π electronic orbitals of these systems can be twofold degenerate, the $E \otimes e$ Jahn-Teller problems for $n = 3, 5, 6, 7$ and the $E \otimes (b_1 + b_2)$ Jahn-Teller problems for $n = 4, 8$ are considered. For these systems, not only linear vibronic coupling but also higher order vibronic coupling with respect to the Jahn-Teller and non-Jahn-Teller active modes was taken into account. As an example, well-known results for the triangular molecule are reproduced in figure 1 and figure 2. Figure 1 shows the APES of the $E \otimes e$ Jahn-Teller system with trigonal symmetry including the higher order vibronic coupling and Figure 2 shows the pseudorotations of the Jahn-Teller deformations.

After investigating the Jahn-Teller effect in the planar molecules, he moves to his study in three-dimensional regular polyhedra such as octahedron, cube and tetrahedron. He first discusses the $E \otimes e$ problem in a similar fashion as for the planar systems. Figure 3 reproduces the well-known picture of pseudorotation of Jahn-Teller deformations in a cube with doubly degenerate electronic state. Further he discusses the systems with triply degenerate T_1 and T_2 electronic states in detail without spin-orbit coupling. He concentrates, in particular, on the $T \otimes (e + t_2)$ Jahn-Teller problems including all quadratic terms. The latter involves the cross terms between e and t_2 vibrational modes as well as the coupling to the bilinear coordinates of e and t_2 vibrational modes. This Jahn-Teller system has two types of minima: the first one after e deformation only and the second, non-trivial one, after both e and t_2 deformations. The pseudorotation of the latter is reproduced below figure 4). Turning to systems with the spin-orbit coupling, Liehr considers the 2T electronic term which splits into Kramers doublet Γ_7 and four-fold degenerate Γ_8 spin-orbit multiplet. He treats the vibronic problem including the couplings between Γ_7 and Γ_8 multiplets, and then focuses on the Γ_8 quadruplet. The latter displays conical intersection at octahedral or tetrahedral symmetry point.

At the end of his analysis of the regular polyhedra, the Jahn-Teller effect in the icosahedral systems (icosahedron and dodecahedron) is also briefly mentioned. At variances to other problems, the form of APES is not derived, only the symmetry of expected extrema after Jahn-Teller active modes is discussed using the "adiabatic correlation" [16]. He predicted that the symmetry of the system becomes as high as D_{5d} or D_{3d} for all degenerate electronic states. Thus he writes:

"The extrema of icosahedral (I_h) potential energy surfaces lie at the six equivalent D_{5d} geometries, the ten equivalent D_{3d} geometries, and the fifteen equivalent C_{2h} geometries..."

Furthermore, he mentioned the possibility that the system can further deform due to the double degenerate electronic states at D_{5d} and D_{3d} points, an assumption which doesn't prove to be true because the ground adiabatic state is already non-degenerate at these symmetry points [17, 18].

Finally, he investigated the irregular polyhedra (mono- and bipyramidal structures). The most important result here is the influence of the spin-orbit coupling on the Jahn-Teller effect. Contrary to the case of regular polyhedra, the spin-orbit coupling lifts the degeneracy of the electronic states, which modifies the radial positions of the minima and make the minima of

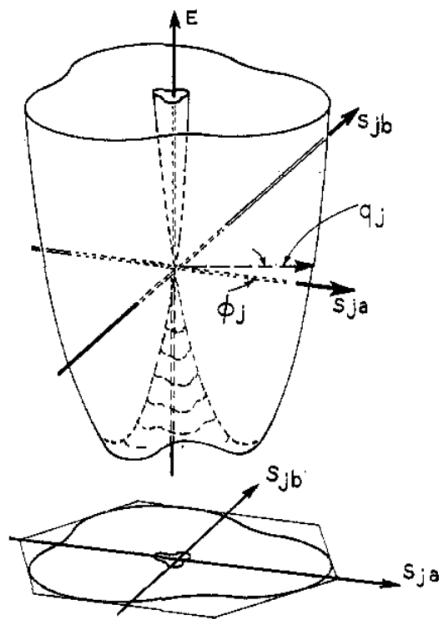


Figure 1. A part of figure 2d from Ref. [1]. The APES of the $E \otimes e$ Jahn-Teller system. S_{ja} and S_{jb} are the $e\theta$ and $e\epsilon$ mass-weighted vibrational coordinates, angle ϕ is the polar coordinates in the space of the e vibrational mode [19].

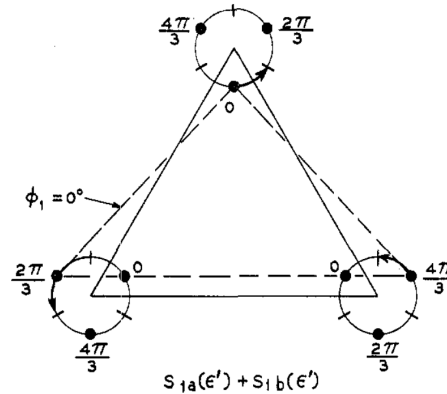


Figure 2. A part of figure 2b from Ref. [1]. Pseudorotation of the Jahn-Teller distortions of $E \otimes e$ Jahn-Teller system with triangular structure. The angles $\phi = 0, 2\pi/3, 4\pi/3$ stand for the position of the minima in the APES.

APES inequivalent (figure 5). The lift of the degeneracy can be predicted based on the group theoretical analysis, the analytical expression giving us better insight into the structure of the APES.

3. Factors defining the structure of Jahn-Teller surfaces

As a summary of his analysis of APES in various Jahn-Teller problems, Andrew Liehr formulates fourteen insights (rules, laws) governing their structure. Many of them remain to be of fundamental importance for the understanding of the Jahn-Teller effect (the numbers below correspond to those in the abstract of Ref. [1]). Below we quote some of them.

The first conclusion concerns the basic group-theoretical technique (descent of symmetry) describing the Jahn-Teller effect:

- 1) *Principle of mathematical inheritance:* the Jahn-Teller-Renner behavior of a polyatomic group theoretic system is completely determined by that of its elemental subgroups.

Further he gives conclusions directly emerging from the group-theoretical analysis:

- 2) *The formation of Jahn-Teller family:* isomorphous point groups exhibit isomorphous Jahn-Teller deportments.

As long as the irreducible representations of electronic wave functions and vibrational modes are the same, we obtain the same Jahn-Teller Hamiltonian and the same type of Jahn-Teller

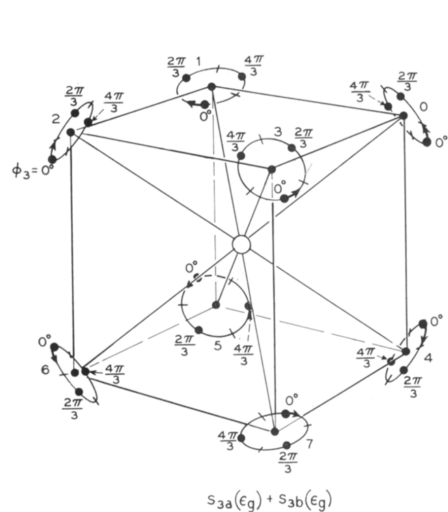


Figure 3. Figure 15c from Ref. [1]. Pseudorotation of the Jahn-Teller distortions of the $E \otimes e$ Jahn-Teller system with cubic structure.

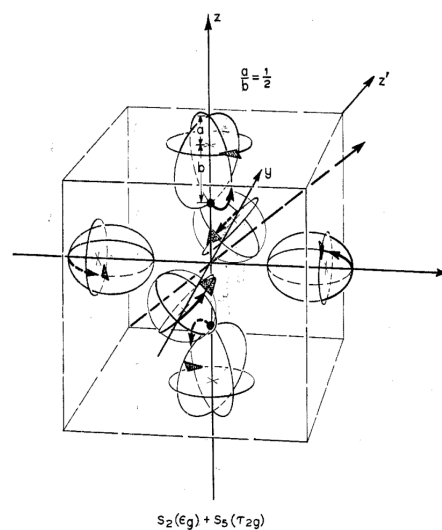


Figure 4. Figure 30a from Ref.[1]. Pseudorotation of the Jahn-Teller distortions of $T \otimes (e \oplus t_2)$ Jahn-Teller system with octahedral structure.

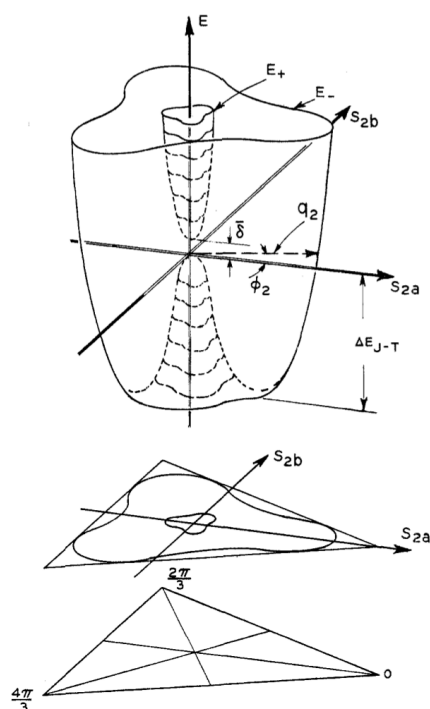


Figure 5. A part of figure 46 from Ref. [1]. The effect of the spin-orbit coupling on the adiabatic potential energy surface of bipyramidal system.

surfaces. Further, as the result of the thorough study of the planar systems, he reaches the next conclusion:

- 3) *Law of prime numbers*: Whereas the prime number groups produce a single unique Jahn-Teller-Renner topography, the non-prime number groups produce all these topographies which are required by the principle of mathematical inheritance (1).

Besides static Jahn-Teller problem, he also addresses general properties of vibronic wave functions:

- 4) *Symmetry transcendence*: The dynamical quantization and the topography of the Jahn-Teller problems are completely specified by group theoretic and permutational symmetry precepts.

Liehr observes that simple analytical solutions for APES are obtained at the symmetry points:

- 6) *Factorization theorem*: the Jahn-Teller-Renner energy resolvants factor only at locations of high nuclear symmetry.

Using these solutions, he draws the information about the shape of the entire APES in several specific cases:

- 12) *Canon of dimensional variability*: Doubly degenerate electronic states possess continuous Jahn-Teller-Renner electronic energy surfaces¹, but triply degenerate electronic states possess disjoint electronic energy surfaces in certain directions.

The complete development of the rule 12) was given later by Pooler [20, 21].

Liehr also discusses the effect of spin-orbit coupling on the APES:

- 9) *Spin-orbit law*: spin-orbit forces remove cuspidal Jahn-Teller radial electronic energy singularities for geometries less regular than the cube.

As mentioned in Sec. 2, he compares the spin-orbit Γ_8 states in cubic system with 2E state in bipyramidal system, and finds that the spin-orbit coupling removes the degeneracy at high-symmetry point in the latter. Such splitting can be understood from the group theoretical analysis, whereas the importance of this statement is due to the analytical expressions which give additional insight.

4. The minimax principle

A special attention deserves the principle put forward by Andrew Liehr as the minimax rule (or minimax law) [1]:

- 5) *Minimax rule*: Although not mathematically required, the symmetry of the stable Jahn-Teller conformation is always the highest symmetry which is yet compatible with the loss of the initial inherent symmetry.

In the summary of the review he formulates his finding in the form of a theorem [2]:

Theorem 2 (Conjectured): The group theoretical symmetry of the stable Jahn-Teller conformation is the highest which is yet compatible with the loss of initial electronic degeneracy.

He emphasizes that this theorem is actually a conjecture made on the basis of available solutions for Jahn-Teller problems and not a rigorous demonstration, at variance, e.g., with the Jahn-Teller theorem (Ref. [1], p. 457):

¹ Liehr uses here the term “continuous” in the sense of “equipotential”, i.e., speaks about the trough at the bottom of the APES.

“...there exist no symmetry arguments which will prevent a molecular system from assuming a structure whose eurythmic elements are those of a subgroup of the total (original) molecular group, which subgroup is of a *lower* order than the minimal order necessary to lift the initial electronic degeneracy. However, from the analytical considerations outlined in this article, it is seen *that a free molecule in a degenerate electronic state will descend in symmetry only as far as the nearest point group which will remove the degeneracy*. This statement can be recast into the following form: *a Jahn-Teller molecule tends to preserve as much symmetry as possible while acting to remove its inherent electronic degeneracy.*”

One should outline clearly the statement contained in the Liehr’s minimax principle. It emerges clearly from the text (e.g., his analysis of the $T \otimes (e \oplus t_2)$ problem as mentioned in Sec. 2) that his minimax principle refers to *the lowest order* of the vibronic coupling sufficient to create minima on the lowest APES of *degenerate* electronic state. Then one should consider two types of Jahn-Teller problems. The first type are the Pooler’s Jahn-Teller problems (or problems with a trough) which arise when the symmetrized square (antisymmetrized square for double valued representation) of electronic irreducible representation (irrep) Γ_0 contains only one single nuclear irrep Γ besides the total symmetric one, A ($[\Gamma_0^2] = A \oplus \Gamma$) [21]. These systems have a trough in the ground APES and the minima can be obtained only by considering quadratic vibronic coupling (examples: $E \otimes e$, $T \otimes h$ and several other Jahn-Teller problems cited in the Pooler’s paper. The second type of Jahn-Teller problems are those in which the symmetrized square of Γ_0 contain more than one low-symmetry nuclear irreps (active nuclear modes): $[\Gamma_0^2] = A \oplus \Gamma_1 \oplus \Gamma_2 \oplus \dots$. In such systems the minima appear in the linear order of vibronic coupling (examples: $E \otimes (b_1 \oplus b_2)$, $T \otimes (e \oplus t_2)$, etc).

In the second type of Jahn-Teller problems, e.g., $T \otimes (e \oplus t_2)$, the minima are realized (depending on the strength of Jahn-Teller coupling to each set of active modes) either in the e -set or t_2 -set of active nuclear vibrations. We emphasize that there are no minima mixing nuclear coordinates of different subsets (e.g., e and t_2) when the linear vibronic coupling only is considered. This is actually a general feature of linear Jahn-Teller problems with several different sets of active nuclear coordinates, which always allows to consider the Jahn-Teller problem with individual subsets when the minima of APES are investigated (e.g., $T \otimes e$ and $T \otimes t_2$ instead of $T \otimes (e \oplus t_2)$). This means that we always deal with Jahn-Teller problems with one single set of nuclear vibrations when investigate the minima of APES, to which the Liehr’s minimax principle perfectly applies.

As mentioned above, the Liehr’s principle is only concerned with the loss of initial electronic degeneracy by the minimal order of vibronic coupling which already provide minima on the APES. Further symmetry lowering due to higher-order vibronic coupling ($T \times (e \oplus t_2)$ problem mentioned in Section 2) including pseudo-Jahn-Teller effect (figure 7.31 in Ref. [22]) will affect only slightly the already existing equilibrium distortion because the lowest-order vibronic couplings (when non-zero) usually give a dominant contribution. The Liehr’s principle concerns precisely these dominant contributions of equilibrium Jahn-Teller distortions.

Despite being conjectured more than half a century ago, this fundamental principle remains valid till our days and became reinforced by new examples of Jahn-Teller problems. One exception from this general rule is the icosahedral $T \otimes h$, where the minima on the lowest APES can correspond to either the highest subgroup D_{5d} (in full accord with the minimax principle) or to the next one, D_{3d} , depending on the sign of the parameter defining the warping of the trough due to quadratic vibronic coupling [23, 24]. The Liehr’s minimax rule has broad connection with the Curie’s principle [25, 26, 27], where the latter states that the greatest common subgroup of the symmetries of the system and perturbations characterizes the resulting effect of the symmetry. Liehr’s minimax rule provides further information on the symmetry of the structure at the minimum of the APES. Thus, the importance of the Liehr’s minimax principle can hardly

be overstated. The distortion of a high-symmetry nuclear configuration can proceed, according to the Jahn-Teller theorem, after any of the non total symmetric nuclear coordinates $Q_{\Gamma\gamma}$ (or their linear combinations) which are contained in $[\Gamma_0^2]$: $\Gamma \subset [\Gamma_0^2]$. As a rule, Γ corresponds to a degenerate irreducible representation and even there can be several different Γ 's entering the $[\Gamma_0^2]$ [19]. This is the reason why the space of Jahn-Teller active nuclear distortions is multidimensional in most Jahn-Teller problems. As a consequence, the possible Jahn-Teller distortions towards a stable electronic configuration represents a multidimensional continuum. The power of the Liehr's principle is that it identifies in this multidimensional space a few directions (corresponding to the highest possible symmetry of the distorted molecule), which *a priori* correspond to stable energy points. The overwhelming fulfilling of the minimax principle in Jahn-Teller problems is of course not accidental and should have a deep physical reason. Its unraveling represents a challenging task for the Jahn-Teller community.

5. Discussion and conclusions

Andrew Liehr was an outstanding scientist pioneering many fundamental aspects of Jahn-Teller effect and its manifestation in real molecules. His major contribution was the investigation of a large variety of static Jahn-Teller and pseudo-Jahn-Teller problems and the identification of the factors defining the basic properties of Jahn-Teller surfaces. Among them, the minimax principle stands out since it represents a statement the importance of which is only outweighed by the Jahn-Teller theorem. Indeed, if the latter proves the structural instability of high-symmetry molecular configurations in orbitally degenerate electronic states, the Liehr's minimax principle tells us how the high-symmetry molecular configurations become distorted. According to Liehr's finding they always tend to preserve the highest symmetry consistent with the loss of orbital degeneracy.

Unfortunately, the research career of Andrew Liehr lasted for only one decade. Despite such a short period of time, he was able to make contributions of fundamental importance which deserve to be remembered, especially what concerns the investigation of Jahn-Teller surfaces, a domain to which Andrew Liehr contributed more than any other.

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